

Appl. No. 10/507,100
Amtd. dated December 30, 2005
Reply to Office action of September 30, 2005
Atty. Docket No. AP928USN

REMARKS

Claims 1, 2, 7, 8, 9, 13, 18, 19, 20, 29, 30, 32, 33, 34, 35, 36, 44, 45, 46, 47 and 49 to 52 are in this application. Claims 1, 2, 9, 13, 18, 19, 29, 30, 32, 35, 44, 45, and 47 have been amended and claims 3 to 6, 10 to 11, 12, 14 to 17, 21 to 28, 31, 37 to 43, 46 and 48 have been cancelled without prejudice. Claims 49 to 52 are new.

To distinguish the invention more clearly with respect to the prior art cited by the examiner and in the International Search Report, independent claims 1 and 32 have been amended to specify that the host matrix comprises a material formed by interpenetrating networks of inorganic and organically-modified phases. Claims 30 and 45 have been amended to reflect the changes to claim 1.

Furthermore, claims 2, 9 and 13 have been combined with other claims as follows:

Claim 2 has been amended to include the limitations of claim 3;

Claim 9 has been amended to include the limitations of claim 10;

Claim 13 has been amended to include the limitations of claims 15 and 17.

Similar changes have been made to the corresponding process claims.

The amendments to the description align the statements of invention on pages 3 and 4 with independent claims 1 and 32, as amended.

In contrast to the disclosures by Chandross *et al.* and Maeda *et al.*, the material of claim 1, as amended, comprises at least two interpenetrating networks of inorganic and organically modified (organic-inorganic) matrixes. In preferred embodiments, the material is created by copolymerization of at least two sol-gel precursors, respectively yielding inorganic and organically modified parts of the network. A strategy of using mutually interpenetrating networks of inorganic and organically modified matrixes and their combination with compatible and highly efficient photopolymerizable, photosensitive and photoinitiating species is an important feature of this invention, yielding a material with unprecedented holographic performance. For example, more than 10 fold improvement in diffraction efficiency, that is a key parameter of a holographic recording material, is achieved compared to the material disclosed by Chandross *et al.*

In contrast to the present invention, the hybrid organic-inorganic matrix disclosed by Chandross *et al* does not contain an independent inorganic network. The latter would obviously require an independent precursor of an inorganic matrix and that is absent in the disclosure by Chandross *et al* . For example, Chandross *et al* teach: "*providing a hybrid inorganic-organic precursor*" (claim 1), not considering an inorganic precursor. Exclusion of an inorganic precursor

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which is inescapable for an inorganic matrix is also obvious from further teachings by Chandross *et al.* For example, they teach that *"the hybrid matrix is typically an oligomer derived from a compound represented by $R_nM(OR')_{4-n}$ where M is a metallic element having a valence of three or higher, such as silicon, titanium, germanium, zirconium, vanadium, or aluminium, R is an alkyl or aryl, R' is a lower alkyl, n ranges from 1 to 2."* An inorganic precursor disclosed in the present application has a general formula $M(OR')_4$, which is not disclosed by Chandross *et al.* Generic composition $M(OR')_4$ obviously requires $n = 0$ in $R_nM(OR')_{4-n}$, whereas Chandross *et al.* limit the range of n from 1 to 2. That Chandross *et al.* do not disclose an inorganic precursor is also evident from further teachings by Chandross *et al.*: *"In an advantageous embodiment, the hybrid matrix precursor is an organosiloxane oligomer derived from hydrolysis and condensation of one or more trifunctional organoalkoxysilanes, e.g. triethoxysilanes"* and also when teaching *"It is also possible to include some difunctional organoalkoxysilanes, e.g. dialkoxysilanes, to provide desired physical properties."* Inorganic precursors disclosed in the present application, in combination with precursors of organically modified part of the interpenetrating network, pertain to a category of tetraalkoxides, namely tetraalkoxysilanes. Use of such precursors is not disclosed by Chandross *et al.*, either generically or in any of their embodiments, and they obviously limit their disclosure to trifunctional and difunctional precursors.

The processes disclosed by Chandross *et al.* have several drawbacks inevitably resulting in a recording material of poor optical and holographic properties rendering it of no practical use for demanding applications such as holographic data storage, as will be explained in the following paragraphs.

Because a hybrid inorganic-organic precursor is used and because inorganic-organic matrixes are known to have inferior mechanical properties compared to inorganic matrixes from inorganic precursors, a curing step is demanded in material by Chandross *et al.* to improve the structural integrity of the matrix. Chandross *et al.* teach: *"curing the mixture to form a hybrid inorganic-organic matrix comprising the photoimageable system, wherein the matrix and the photoimageable system exhibit independent chemistries"* (claim 1). The curing inevitably results in some premature polymerization of the photoimageable system, that in turn inevitably degrades the holographic properties. In this regard Chandross *et al.* teaches: *"Due to the effect of the pre-cure, the final cure is typically performed at a relatively low temperature of about 60 to about 80 degrees C, for a relatively long period of time, e.g., over 50 hours. This temperature range is sufficient to continue the condensation started during the pre-cure, but generally low enough to reduce premature polymerization of the photoactive monomer in the photoimageable system. A complete cure of the siloxane matrix is not required to form a usable medium. As discussed generally above, a cure of about 80% is typically adequate to provide the desired structural integrity."* It is known that

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mechanical properties of hybrid inorganic-organic matrixes based on trifunctional and/or difunctional precursors, to the category of which belongs the material disclosed by Chandross *et al*, are poor and such matrixes are mechanically fragile and prone to cracking that can destroy the structural integrity of the matrix. This problem becomes particularly acute when the matrix is used in holographic recording, during which it is subject to large internal forces that accompanies polymerization of the photoimageable system. This problem is further exacerbated in the process taught by Chandross *et al* where a complete cure (and hence full matrix densification) is disclosed to be avoided in order to minimize the effect premature polymerization of the photoimageable system. In contrast to the process by Chandross *et al* where the matrix is not fully cured to reduce premature polymerization, high level of matrix cure (densification) is required to guarantee sample structural integrity not only during hologram recording but also in fabrication steps such as optical grade polishing. The latter is required when the sample is used as a bulk monolith rather than a film to yield a larger data storage density based on Bragg multiplexing for which bulk samples are preferred.

Another disadvantage of Chandross *et al* material is that, in order to be able to use cures at a relatively low temperature (to avoid premature polymerization of the photoimageable system), pre-cure is required. Chandross *et al* teach: "*A pre-cure is advantageously performed on the oligomeric organosiloxane precursor. Before and during the precure, portions of the solvents and condensation products, which are generally volatile, typically evaporates. The precure is generally performed at a temperature of about 100 to about 160 degree C for a relatively short time period of about 10 minutes or less. The pre-cure promotes further condensation of the oligomer precursor, thereby raising the viscosity.*" It is known that such condensation and the viscosity increase are due to increasing size of the condensed clusters and particulates (conglomerates) that in turn degrade optical quality of the matrix because the light is scattered on such conglomerates. Also miscibility with the photoimageable system is worsen, which in turn degrade optical properties because of the scattering when the constituting elements are not mixed together at molecular level due to their limited miscibility. Highest possible miscibility (at molecular level) is required for best optical quality to alleviate the scattering problem. Low levels of light scattering are known to be a fundamental requirement for a photoimageable material to be useful in demanding applications such as holographic data storage. The light scattering is particularly acute in samples of large thickness which are needed for Bragg multiplexing, where even a modest level of scattering can be unacceptable as it can result in crosstalk and loss of data.

Chandross *et al* further teach: "*The pre-cured organoalkoxysilane matrix precursor is typically mixed with solvent to lower the viscosity, in order to promote mixing with the photoimageable system. As mentioned previously, the bulk of the solvent is then removed by heating*

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gently under vacuum, which also drives the matrix condensation further." Hence, additional heating step is needed, unavoidably resulting again in some polymerization reaction of the photoimageable system. Such premature polymerization further deteriorates holographic properties, namely limits dynamic range and hence the ultimate achievable data storage density when the material is used in a holographic data storage application.

A serious drawback of the process by Chandross *et al* is that, because of the fragile nature of the organic-inorganic matrix that is a generic property of hybrid matrixes made from trifunctional and bifunctional precursors, such as those taught by Chandross *et al*, it is practically impossible to fabricate samples in the form of bulk monoliths polishable to a highest optical quality and resistant enough to avoid cracking when large forces are exerted upon a matrix by the photoimageable system during the polymerization of the latter upon hologram recording. To partially overcome at least the problem how to physically fabricate the sample as the optical quality of bulk sample would be poor, Chandross *et al* teach: *"Fabrication of the recording medium typically involves depositing the matrix precursor/photoimageable system mixture between two plates using, for example, a gasket to contain the liquid mixture. The plates are typically glass, but it is also possible to use other materials transparent to the radiation used to write data, e.g., a plastic such as polycarbonate or poly(methylmethacrylate)."* However, it is known that in such arrangement the polymerization-induced shrinkage that is inevitably present during the holographic exposure would have a detrimental effect on the optical properties of the medium. This is acknowledged by Chandross *et al*, when teaching: *"During the matrix cure, it is possible for shrinkage in the material to create stress in the plates, such stress altering the parallelism and/or spacing of the plates and thereby detrimentally affecting the medium's optical properties."* In practice it is extremely difficult, if not impossible, to eliminate these detrimental effects. Chandross *et al* teach: *"To reduce such effects, it is useful to place the plates in an apparatus containing mounts, e.g. vacuum chucks, capable of being adjusted in response to changes in parallelism and/or spacing. In such apparatus, it is possible to monitor the parallelism by use of a conventional interferometric method, and make any necessary adjustments."* This process requires implementation of additional apparatus (interferometer + vacuum system + actuators required for parallelism and/or spacing adjustment) in the holographic recording system. Furthermore, the effectiveness of the disclosed process is dubious as the process gives little margin for adjusting the spacing and parallelism without compromising the structural integrity of the sample when the compensatory forces are applied by the external actuators.

All the drawbacks outlined above are eliminated in embodiments of the present invention. In contrast to the disclosure by Chandross *et al*, the matrix of the present invention comprises at least two interpenetrating networks of inorganic and organically modified (organic-inorganic) matrixes,

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of which at least one is inorganic (cf. claim 1). An independent inorganic matrix combined with an organically modified matrix provides excellent optical, holographic, and mechanical properties, as required for demanding applications such as holographic data storage. These include high structural integrity, ability to prepare samples of large optical thickness in film or bulk format, high optical quality, low scattering noise, and excellent holographic properties. A further key feature of embodiments of this invention is the process of copolymerization, advantageously of epoxysilanes and either or both of a tetraalkoxysilane and a trialkoxysilane (cf. claim 19), and the material resulting thereof. While tetraalkoxysilanes substantially improves mechanical properties, such as hardness, epoxysilanes markedly improve the structural integrity of the matrix providing excellent resistance to cracking. Another key feature is the use of triethoxysilane $R'Si(OR)_3$ or diethoxysilanes $RR''Si(OR)_2$ as the precursor with R' and R'' being a polymerizable group such as an epoxy group, and incorporation of original and highly efficient photoinitiator in combination with suitable monomers. All these findings results in a process yielding a material with markedly improved holographic performance compared to previous art, and especially Chandross *et al*'s disclosure. Diffraction efficiency (a key holographic parameter) close to a theoretical 100% is readily achieved in material embodying the present invention compared to 8% disclosed by Chandross *et al* (shown in Figures 8 and 9 Chandross *et al*'s patent).

Optically recording films disclosed by Maeda *et al.* are fundamentally different from material embodying the present invention. In contrast to material defined in claim 1, comprising at least two interpenetrating networks of inorganic and organically modified matrixes, the matrix by Maeda *et al.* is strictly an *inorganic* substance. Maeda *et al* teach [0018]: "*According to the present invention, there is provided an optical recording film comprising a gel having a network structure of an inorganic substance and a polymer which is from a photopolymerizable compound (A) and present in the network structure of the gel, said gel containing an optical recording-induced difference in the network structure of the gel.*" The inorganic nature of the network is one of the key teachings of Maeda, *et al* as it is found e.g. in Abstract (1,2,3), and further in [0018], [0019], [0022], [0023], [0024], [0029], [0030], [0031], [0038], [0042], [0043], [0061], and so on, including all the examples. Maeda *et al* further teach: "*The inorganic substance includes metal oxides such as silicon oxide, titanium oxide, zirconium oxide, and aluminium oxide. Of these, silicon oxide and titanium oxide are preferred.*" On the precursors of the matrix, Maeda *et al* teach: "*Specific examples of the metal alkoxide preferably include tetraethoxysilane, tetramethoxysilane, tetrabutoxysilane, titanium tetrakisopropoxide, titanium tetrabutoxide, zirconium tetramethoxide, zirconium tetrabutoxide, and aluminium triethoxide.*" All the precursors disclosed by Maeda *et al* are known to yield a gel with inorganic structure, as is acknowledge by Maeda *et al* at various points of their disclosure.

Inorganic gel matrixes, to which category Maeda *et al*'s optical recording film belongs, are

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known to have a number of drawbacks. First, large internal stresses accompanying large material shrinkage during preparation of an inorganic gel inevitably result in cracking of thick films that sets the ultimate limit on maximum achievable film thickness that is typically in the micrometer range. This thickness range is not sufficient for holographic data storage application. It is known that inorganic gel matrixes cannot be prepared in thicknesses on the order of several hundreds of micrometers. These material thicknesses are required in applications such as holographic data storage relying on Bragg multiplexing of multiple holograms in the same spatial location that in turn demands a thick recording material, typically about 200 micrometers or more. Meada *et al* apparently are aware of the thickness limitation of their inorganic films, since they state: "*The thickness of the film for optical recording is generally 0.01 to 100 microns, preferably 1 to 30 microns.*" This range of thicknesses is not sufficient for applications in holographic data storage.

Second, material shrinkage is known to be very large in inorganic gels, to the category of which belong the materials disclosed by Maeda *et al*. Mitigating the material shrinkage is one of the fundamental challenges in development of recording materials for application in holographic data storage. Material shrinkage during or after holographic exposure causes distortions in the hologram planes that can result in irretrievable loss of data, or crosstalk problems. In holographic data storage, it must be assured that the shrinkage is very low, typically less than a fraction of a percent. Maeada *et al* teach: "*In the above step of removing the organic components, the optical recording film is rendered porous, and the film shrinks in the thickness direction so that it has a thickness of approximately 1/2 and 1/20.*" This exceeds more than two orders of magnitude the shrinkage tolerance typically required for holographic memories, rendering the material by Maeda *et al* of no use for demanding applications such as holographic data storage.

It appears that fundamental to the disclosure by Meada *et al* is that the hologram is based on network modification, namely network density modification. Maeda *et al* teach: "*A network structure difference is present in the gel constituting the first optical recording film of the present invention, and optical recording is based on the difference. For example, the gel contains coarse network portions network portions, and optical recoding is based on this coarse-dense distribution.*" This is achieved, as Maeda *et al* teach, by the following mechanism: "*During the polymerization, part of the network of the inorganic substance initially present in a high light intensity portion is pushed away into an adjacent low light intensity portion by a polymer whose volume has grown due to photopolymerizable compound (A) supplied from a low light intensity portion.*" However, as it is explained below and also acknowledged by Maeda *et al*, this mechanism of pushing the inorganic substance from the high light intensity region into an adjacent low light intensity regions acts in an opposite direction than the diffusion of the photopolymerizable compound, hence it decreases the achievable hologram refractive index modulation and hologram diffraction efficiency. It is known

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in the art (as Colburn-Haines mechanism) that photopolymerizable substance diffuses from the low light intensity regions to the high light intensity, also acknowledged by Maeda *et al* when saying: *"That is, the polymerization starts at a portion where the light intensity is high, and photopolymerizable compound (A) is accordingly consumed. Therefore, photopolymerizable compound (A) is supplied from a portion where the light intensity is low to a portion where the light intensity is high, and the polymerization is further promoted."* This diffusion of the monomer in one direction and pushing away the network in the contrary direction inevitably reduces the photoinduced material density changes, hence lowers refractive index modulation and hologram diffraction efficiency. In material embodying the present invention, contrary to material by Maeda *et al*, the photoinduced refractive index changes are due to monomer diffusion and polymerization whereas the matrix changes are minimized in the matrix of the present invention with two interpenetrating networks. In part to alleviate the problem of low diffraction efficiency in their first optical recording films, Maeda *et al* disclose removing the organic component, so that only the network density changes remain. In this respect, Maeda *et al* teach: *"The second and third optical recording films can be obtained by removing organic components from the first optical recording film"* to obtain, as they teach: *"A porous gel having a network structure of an inorganic substance, and it is an optical recording film in which a network portion having a high porosity and a network portion having a low porosity are present in the porous gel, those different porosities being induced by an optical recording."* It is known in the art that organic components can be removed from an inorganic gel matrix by heating. This also is acknowledged by Maeda *et al* when saying: *"The organic components can be removed, for example, by a method in which the film is heated up to 200 degrees C or higher. In this heat treatment, the organic components in the optical recording film are removed from the film by oxidation and decomposition, and portions from which the organic components have been removed remain as pores, in which gasses such as air are present. The temperature for the above heat treatment depends on the organic compounds to be removed such as the photopolymerizable compound (A) and a solvent. For increasing the denseness and mechanical strength of the optical recording film, it is preferred to heat the film up to high temperature."* This technique has two evident drawbacks. First, by burning the organic components, a portion of the burned by-products is inevitably trapped in the matrix deteriorating optical quality of the later, namely absorption and scattering that both are detrimental in demanding applications such as holographic data storage. Scattering properties can be further deteriorate by heat-induced formation of silica particles that act as the scattering centers. Formation of silica microparticles has been acknowledged by Maeda *et al* thus: *"It was found that silica particles (diameter approximately 0.01 - 0.1 microns) were densely present inside convex portions on the film surface and they were coarsely present (there were many pores) in concave portions."* Another drawback of this technique,

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as already discussed above, is that the heating inevitably results in material shrinkage which is typically two orders of magnitude larger than shrinkage acceptable when the material is aimed to be used as a holographic storage medium.

Because of the above reasons, the inorganic matrix disclosed by Maeda inevitably results in poor holographic properties, including low diffraction efficiency. For example, the highest diffraction efficiency disclosed by Maeda *et al* is about 50%, and even to achieve this moderate figure, heating at a large temperature (400 degrees C) is required. In material according to the present invention, diffraction efficiencies close to 100% theoretical maxima are routinely achieved and heating at high temperature is avoided together with the negative consequences of such treatment, namely poor optical quality, scattering and absorption losses, and shrinkage.

Thus, whether taken individually or in combination, the disclosures by Cahnngross *et al* and Maeda *et al* neither disclose nor suggest the present invention, and would not motivate a person skilled in this art to modify their teaching to arrive at the material and process of the present invention.

In view of the foregoing, it is submitted that all claims of record are patentable over the cited references and early and favourable reconsideration of the application is respectfully requested.

Respectfully submitted,



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